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Transition metal doped ZnS nanoparticle systems and their response to swift heavy ion irradiation

U Das[1], D Mohanta[1]*, F Singh[2], A Tripathi[2], D K Avasthi[2] and A Choudhury[1]

[1]Department of Physics, Tezpur University, Napaam, Assam-784 028, Assam, India
[2]Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110 067, India

E-mail : best@tezu.ernet.in

Abstract : Transition metal (Cr) doped ZnS nanoparticles were fabricated by adopting a solution growth-chemical route. They were irradiated by 150-MeV titanium ion beams using tandem pelletron accelerator available at IUAC, New Delhi. Irradiation led manifestations in luminescence patterns and morphology has been discussed in analogy with modification in magnetic domains. The present study would find promising application in magnetic sensors and spintronics devices.

Keywords : Nanostructures, luminescence, ion irradiation.

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1. Introduction

Semiconductor nanostructures, which use the principle of three dimensional carrier confinement, have emerged as important technological assets for their dimensional dependent optoelectronic properties. The nanoscaled systems exhibit quantum size effect thus, inducing quantization of the bulk electronic bands into discrete electronic states. This leads to size dependent electronic and optical properties of nanoparticles [1–4]. The fact that the band gap of the material varies with the crystallite size which makes them an interesting category of materials for potential application in novel devices. Among binary semiconductor systems, ZnS is the most widely investigated system having a direct band gap of 3.7 eV at room temperature. It is an important phosphorescent material both in doped and un-doped form. It has been established that when doped with some magnetic impurities, these nanostructures develop a unique class of material called diluted magnetic semiconductors (DMS) which are promising candidates for magnetic memories, sensors and other spin-based devices [5,6]. Such semimagnetic and semiconducting structures, where carrier and spin confinement is possible provides a matchless system for spin manipulation and spin transportation [7]. Again, swift heavy ion irradiation is a useful tool for the development of nanostructures

*Corresponding Author

through ion implantation, ion beam mixing and template synthesis *etc.* [8–12]. In this particular report, we highlight impact of 150-MeV Ti^{11+} ions on the photoluminescence and morphological changes in polymer encapsulated ZnS:Cr nanostructures. Further, significant modification in magnetic domains has also been discussed.

2. Experimental

First, 5% (w/v) transparent polyvinyl alcohol (PVOH, 1 mw) matrix was prepared under moderate stirring (~200 rpm) and heating (65°C) for 3 hours. Next, 0.15 M $ZnCl_2$ was added to the PVOH matrix under stirring environment and the precursor was kept at ice cold temperature. Then, 0.0066 M Cr_2O_3 solution at 100°C was quenched into the as-prepared precursor. The whole solution was left undisturbed overnight. Next, H_2S gas was allowed to diffuse through the solution for maximum absorption and result Cr doped ZnS nanocrystals. Nanocrystalline films are casted on 1 × 1 cm^2 laboratory slides for the irradiation experiments.

The irradiation was carried out on four identical samples. The nanoparticle samples were mounted on a vacuum shielded vertical sliding ladder having four rectangular faces. One sample was reserved as virgin to compare with the irradiated ones. They were irradiated at high vacuum (1.6×10^{-6} torr) by 150-MeV Ti^{11+} beam with approximated beam current 1.0 pnA (particle nano ampere). The fluence was varied in the range 10^{10} to 10^{12} ion/cm^2. In order to expose the whole target area, the beam was scanned vertically over the sample plane. The energy of the ion beam was chosen in such a way that the projectile range of the incident ion (21.3 μm, as computed by SRIM program [13]) exceeds thickness of the sample films ~0.5 μm). Again, the ion beam energy and thickness of the target was selected so that modification due to electronic energy loss (S_e) affects the sample. Energy dependent electronic energy loss (S_e) and nuclear energy loss (S_n) for Ti-ions is shown in Table 1.

Table 1. Energy loss *vs.* projectile range [13].

Energy MeV	Electronic energy loss $S_e = (dE/dx)_e$ eV/Å	Nuclear energy loss $S_n = (dE/dx)_n$ eV/Å	Projectile range R (μm)
10^{-2}	1.53	18.99	.0419
10^{-1}	5.03	20.59	.2913
1	25.47	8.59	.2820
10	109.75	1.76	1.446
100	512.37	0.23	15.26
150	587.29	0.17	21.32

3. Results and discussion

The X-ray diffraction pattern of ZnS nanoparticles is shown in Figure 1. It depicts cubic crystalline structure corresponding to three diffraction peaks (111), (220) and (311) at 27.5°, 46.2° and 56°, respectively. The broadening in the diffraction peak corresponds to the formation of nanoparticles. The average particle size estimated is ~10 nm,

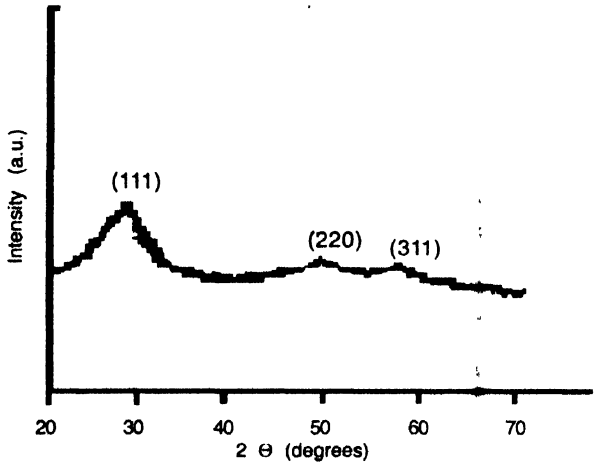

Figure 1. XRD pattern of ZnS nanoparticle.

obtained by measuring full-width-at half maxima (FWHM) and using Scherrer's formula $d = 0.9\lambda/w\cos\theta$.

Normally, the photoluminescence study provides information relating to different energy states available between valence band and conduction band responsible for radiative recombination. It is well known that when emission peak energies are less than the band gap energy of the material, these bands ascribe to transition involving donors, acceptors, free electrons and holes. The appearance of the PL peak with energy close to the band gap energy suggests band edge emission [14]. It has been studied that the photoluminescence efficiency of coated ZnS:Mn nanoparticle is higher than the powder sample due to passivation of surfaces [15]. In addition to Mn^{+2} yellow-orange emission, irradiation led surface emission enhancement in ZnS:Mn nanoparticles has been reported by our group very recently [16]. A Cr-related near-infrared photoluminescence (PL) band in ZnSe with a main no-phonon line at 10702.2 cm^{-1} has previously been reported [17]. Crystal field calculations demonstrate that the observed no-phonon lines and the corresponding luminescence band can reasonably be interpreted in terms of a $^3T_L(H) \rightarrow {}^5T_2(D)$ transition within the d^4 configuration of Cr^{2+} [16]. Similarly, Luo have extensively studied the effect of incorporation of Cr into epilayers of ZnTe, developed by molecular beam epitaxial method [18]. They observed that Cr^{+2} ions produce a broad emission peak in the IR-regime 2–3 μm. The temperature dependent luminescence studies have also been performed by them to determine thermal quenching activation energies.

Figure 2 represents PL response of pristine and ion irradiated ZnS:Cr nanostructures. It depicts three distinct bands around 475 nm, 540 nm and 700 nm. We ascribe the emission peak ~475 nm as donor-acceptor (D-A) pair transition and the band at ~700 nm corresponds to surface state fluorescence activation due to nano-ZnS, in consistency with our recent work in ZnS:Mn systems [19]. However, the blue-green emission peak at ~540 nm is expected due to *d*-electron transfer of Cr ions into the

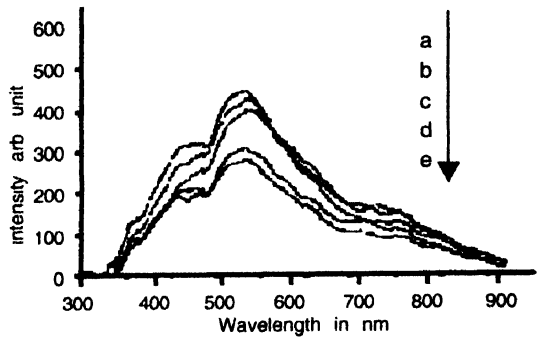

Figure 2. PL emission spectra of (a) unirradiated and irradiated, (b) 5×10^{10}, (c) 2×10^{11}, (d) 8×10^{11}, (e) 3.2×10^{12} ions/cm^2 ZnS: Cr nanoparticles.

ZnS host. Strong Cr-emission dominates the fluorescence activation as well as emission due to D-A pair transitions to the extent that the heavily exposed sample also possesses significant emission band ~540 nm. The PL peaks decrease in intensity with the increase in ion dose, possibly due to suppression in recombination emission owing to grain growth phenomena under ion irradiation.

It has been found that V or Cr doped ZnS, ZnSe, ZnTe are ferromagnetic, without p-type or n-type doping treatment. However, Mn, Fe, Co, Ni substituted ZnS, ZnTe *etc.* are found to be in spin glass states [20]. To exploit magnetic properties, we have carried out magnetic force microscopic studies on irradiated ZnS:Cr nanosystems, represented in Figure 3. The figures are basically phase images of the magnetic impurity (Cr) doped ZnS nanostructures. Figure 3a is the phase image of the pristine

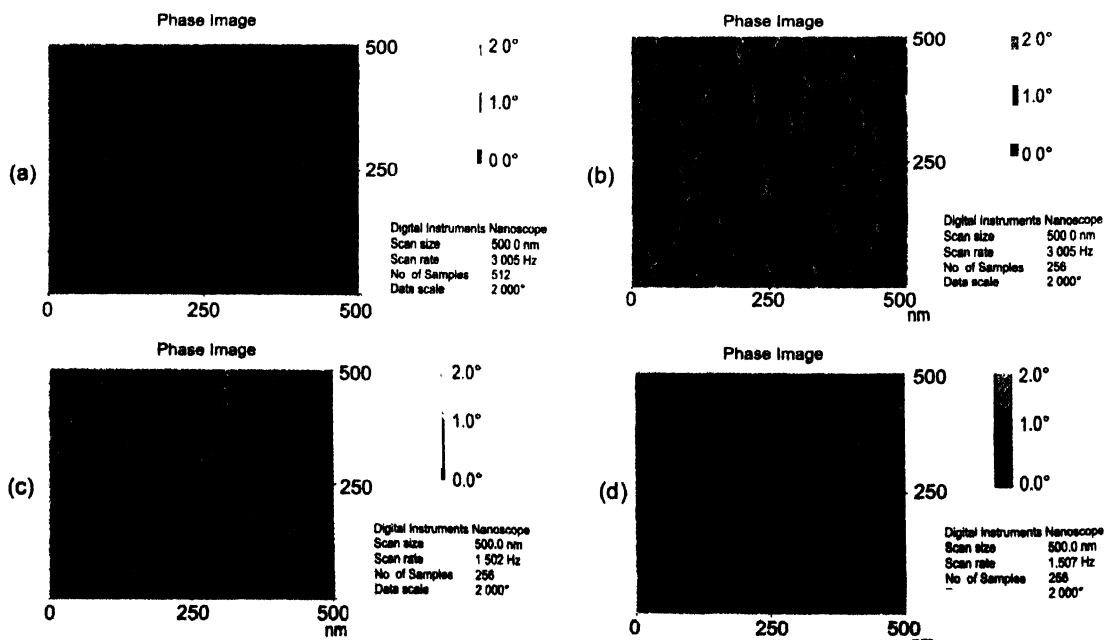

Figure 3. MFM images (200 × 200 nm) of (a) unirradiated and irradiated, (b) 5×10^{10}, (c) 2×10^{1}, (d) 8×10^{11}ions/cm^2 ZnS:Cr nanoparticles.

ZnS:Cr, which does not show appreciable results on the magnetic domains owing to matrix encapsulation, which prevents from detecting magnetic domains by the tip of the MFM. Figure 3b is the sample irradiated at 2×10^{11} ions/cm^2 where spherical single domains (~30 nm) are visible which correspond to ZnS:Cr nanoparticles distributed uniformly in the matrix. Irradiation with fluence 4 times leads to distorted domains, shown in Figure 3c. Surprisingly, sample exposed at 3.2×10^{12} ions/cm^2 results in the aligned magnetic domains normal to ion trajectories. These aligned domains in which elongation upto ~200–250 nm has been observed would find application in magnetic tapes, magnetic recording devices and other spin-based devices.

5. Conclusion

In conclusion, we have produced Cr doped ZnS nanostructures by simple and inexpensive chemical route. Photoluminescence shows a new emission peak around ~540 nm due to Cr^{+2}. The low ion fluence recovers the nano-ZnS:Cr from matrix encapsulation and affect the shape of the magnetic domains. Spherically distributed domains turn into elongated domains upon ion impacts possibly, due to pressure led development of structural elongation normal to the ion trajectories.

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